

Upgrading of Rice Husk by Torrefaction and its Influence on the Fuel Properties

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Torrefaction refers to thermal treatment of biomass at 200 to 300 °C in an inert atmosphere, which may increase the heating value while reducing the oxygen content and improving the storability. In this study, the effects of torrefaction temperatures on the properties of rice husk were analyzed. Torrefaction experiments were performed using a lab-scale device designed to reduce heat and mass transfer transient effects. A new method is described for clarifying torrefaction time and minimizing experimental error. Results from analysis of torrefaction temperatures (200, 230, 260, and 290 °C) support the supposition that the fiber structure is damaged and disrupted, the atomic oxygen ratio is reduced, the atomic carbon ratio and energy density are increased, the equilibrium moisture content is reduced, and the hydrophobic properties of rice husk are enhanced. The data presented in this paper indicate that torrefaction is an effective method of pretreatment for improving rice husk. Torrefaction at 230 to 260 °C for 30 min was found to optimize fuel properties of the torrefied rice husk.

Keywords: Biomass; Rice husk; Torrefaction; Fuel properties; Grindability

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INTRODUCTION

Biomass has been recognized as a clean and renewable energy source. The thermo-chemical conversion utilization of biomass is gaining increasing attention (Chen *et al.* 2014). In 2012, the yield of rice husk in China was estimated to be 41 million tons, accounting for about 28.6% of the total output of the world, according to the Food and Agriculture Organization of the United Nations (FAO). Rice husk is a very important biomass raw material for thermo-chemical conversion. It is extensively used in pyrolysis and gasification. However, the properties of raw biomass, such as its high oxygen content, high moisture, low calorific value, large particle size, and grinding difficulty, have limited the further development of biomass application technology (van der Stelt *et al.* 2011; Chen *et al.* 2012a; Yin *et al.* 2012). Moreover, in order to avoid the CO₂ costs related to transportation, leading to greater end-use efficiency, bioenergy should be generated in the same locale where biomass is produced (Protasio *et al.* 2013). Also, the selection of an appropriate pretreatment approach is understood to be the key to addressing biomass defects.

Compared with drying pretreatment (room temperature to 150 °C), torrefaction pretreatment at 200 to 300 °C can better improve biomass quality (Chen *et al.* 2012b). Torrefaction is a thermal treatment with the reaction temperature between 200 and 300

°C under the conditions of ordinary pressure in the absence of oxygen (Shang *et al.* 2013; Zheng *et al.* 2013). This moderate thermal process breaks down the fiber structure of biomass, so that biomass becomes easier to grind (Arias *et al.* 2008; Chen and Kuo 2010; Phanphanich and Mani 2011).

The improved biomass structure also contributes to the liquidity of biomass materials in a gasification reactor (Deng *et al.* 2009). In addition, it can effectively reduce the oxygen content, enhance biomass energy density, improve the C/O ratio, and reduce the transportation and storage costs of biomass (Wannapeera and Worasuwanarak 2012; Patuzzi *et al.* 2013).

Hemicellulose has a large capacity to absorb humidity, and a large proportion of it can be degraded and released as gaseous byproducts in the course of torrefaction. As a consequence, biomass becomes more hydrophobic, and the water is not as easily absorbed by the biomass again (Yan *et al.* 2009; Acharjee *et al.* 2011). Currently, studies on torrefaction preprocessing have achieved a certain amount of progress, but almost all studies have been targeted at wood as a raw material (Arias *et al.* 2008; Wannapeera *et al.* 2011; Peng *et al.* 2013; Ren *et al.* 2013; Sabil *et al.* 2013; Tran *et al.* 2013). There are few reports available in the literature regarding torrefaction of rice husk. Therefore, the first objective of this work is to study the effects of torrefaction on the fuel properties of rice husk.

In addition, experimental methods of biomass torrefaction should also be improved. Previous studies often adopt the method of heating biomass from room temperature to torrefaction temperature and then maintaining the torrefaction temperature for a specified time (Arias *et al.* 2008; Wang *et al.* 2011; Medic *et al.* 2012; Rousset *et al.* 2012; Shang *et al.* 2013). However, this approach makes it difficult to precisely determine torrefaction time and the torrefaction mechanism.

The period of biomass heating (about 10 to 30 min) cannot be simply included in the torrefaction process because in this period, the sample temperature does not reach the required torrefaction temperature. However, this period of slow temperature rise should also not be ignored, because the structure of biomass has been changed and organic components begin to decompose, which leads to inaccurate results in the analysis of changes to the physical and chemical properties of biomass. Also, at the end of the experiment, the sample temperature remains high in the torrefaction device (*e.g.*, tube furnace) and the decomposition continues, leading to a relatively low yield of solid products.

Thus, the second objective is to present a testing method that allows the biomass sample to quickly reach the set torrefaction temperature at the beginning of the experiment and quickly cool at the end of experiment, to enable the changes to the physical and chemical properties of biomass to happen at torrefaction temperature.

This article focuses on the effect of torrefaction temperature on fuel properties. A torrefaction testing method was developed to rapidly heat the biomass samples and to reduce the transient effects of heat-up rate and mass transfer of devolatilized products. The fuel properties of rice husk, such as proximate analysis, ultimate analysis, component analysis, heating value, hydrophobic properties, and grindability, were studied. Detailed process design and cost-benefit analysis are beyond the subject of the research, and they will be discussed in subsequent studies.

EXPERIMENTAL

Materials

Rice husk selected from suburb of Hefei city was used as raw material in this study. The raw rice husk (RH) had a moisture content of 9.4% (dry base). Rice husk was dried for 6 h at 110 °C, and the dried rice husk (DRH) were stored in a quartz dryer for further use.

Methods

A lab-scale torrefaction device, which was developed by the authors, is shown in Fig. 1. Before the experiment, rice husk (5 g) was placed in a feedstock container. A temperature controller was used to control the experimental temperature. A heating furnace, with an outer thermal insulation coat, heated a quartz reactor. When the temperature was reached and stabilized at the experimental temperature, the samples were fed from the glass feedstock container into the downstream quartz reactor. Quartz wool with stainless steel wires was used to support the samples and enhance the heat transfer effect to allow the rice husk to rapidly reach the experimental temperature. The temperature of the sample was determined by a thermocouple and recorded every one minute (recorded every 0.25 min in the first 2 min). The samples were torrefied for 30 min with a flow rate of 500 mL/min of nitrogen. Soon after the volatile gases left the reactor, they were condensed, and liquid products were collected in a condenser. The non-condensable gases were collected by a gas collecting bag every few minutes. After the experiment, the heating furnace was opened and the contents were moved out the quartz reactor. The reactor was quickly cooled by forced convection using a blower, and the flow of nitrogen was constantly maintained until the sample temperature dropped below 100 °C. In this study, the rice husk was torrefied at 200, 230, 260, and 290 °C for 30 min, respectively. Each test was repeated three times under the same conditions.

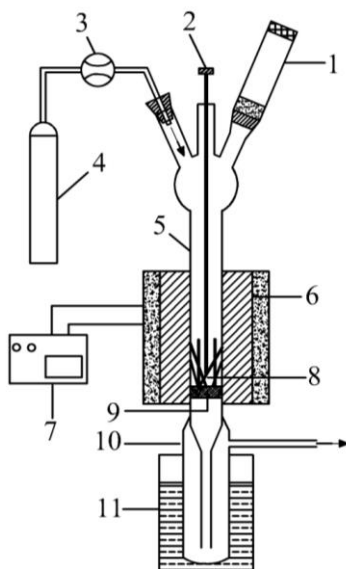


Fig. 1. The lab-scale torrefaction device; (1) Feedstock container, (2) Thermocouple, (3) Flowmeter, (4) Nitrogen cylinder, (5) Quartz reactor, (6) Heating furnace, (7) Temperature controller, (8) Stainless wires, (9) Quartz wool, (10) Condenser, (11) Liquid nitrogen container

Sample Labels

The torrefied rice husk was denoted TRH-X, with the value of “X” indicating the torrefaction temperature (in °C). For example, a run labelled TRH-230 corresponds to torrefaction of rice husk carried out at 230 °C during 30 min.

Solid Yield and Energy yield

The HHV can only reflect the energy changes *per* unit mass of torrefied rice husk, but mass changes to rice husk during torrefaction are not considered. Solid yield and energy yield are two important parameters used to evaluate the effects of biomass torrefaction. The definition of solid yield and energy yield are as follows,

$$Y_{\text{mass}} = \frac{M_{\text{product}}}{M_{\text{feed}}} \times 100\% \quad (1)$$

$$Y_{\text{energy}} = Y_{\text{mass}} \frac{HHV_{\text{product}}}{HHV_{\text{feed}}} \quad (2)$$

where Y_{mass} and Y_{energy} stand for solid yield and energy yield, respectively. The subscripts “feed” and “product” stand for the dried rice husk and solid product after torrefaction (torrefied rice husk), respectively. The units of M_{product} , M_{feed} , HHV_{product} , and HHV_{feed} are kg, kg, MJ/kg, and MJ/kg, respectively.

Analysis of Fuel Properties

Proximate analysis of samples was performed according to the D3172-07a standard. Ultimate analysis was carried out using an elemental analyzer with an instrument precision of <0.5% (Vario macro cube, Elementar, Germany), and oxygen was estimated by the difference: O(%) = 100% - C(%) - H(%) - N(%) - S(%) - Ash(%). The heating value was measured in an adiabatic oxygen bomb calorimeter with an instrument precision of ≤0.2 % (XRY-1A, Changji Geological Instruments, China).

The contents of hemicellulose, cellulose, and lignin in biomass were determined by the modified Van Soest method (Yan *et al.* 2009). In brief, the rice husk was dried and treated in a neutral detergent solution first. The difference of rice husk and the neutral detergent fiber (NDF) was the extractives content. Then, the sample was digested with acid-solution, and the acid detergent fiber (ADF) was determined. Acid detergent lignin (ADL) was measured by further treating ADF with 72% H₂SO₄. The contents of hemicellulose, cellulose, and lignin were calculated from the difference of NDF, ADF, ADL, and ash.

To evaluate the grindability of dried and torrefied rice husk, the samples were ground in a mill with a sieve of 16 mesh (1mm) for 1 min and then sieved into five fractions, including 16 to 40 mesh (1 to 0.38 mm), 40 to 60 mesh (0.38 to 0.25 mm), 60 to 80 mesh (0.25 to 0.18 mm), 80 to 140 mesh (0.18 to 0.109 mm), and 140 to 400 mesh (0.109 to 0.038 mm). The particle size distribution was evaluated by the weight percentage of each fraction.

To evaluate the hydrophobic properties of torrefied rice husk, the equilibrium moisture content (EMC) was measured using a constant temperature and humidity incubator with temperature precision of ≤2 °C and humidity precision of ±4% R.H (SPX-250 °C, Shanghai Boxun, China). The torrefied samples (3 g) were exposed to an environment with constant humidity and temperature (30 °C, relative humidity 50%) over

a long period of time (more than 7 days), until the sample mass was constant for three consecutive days. Then, the samples were dried at 110 °C for 6 h, and this moisture content was considered the EMC.

RESULTS AND DISCUSSION

Temperature Profiles of the Samples

Figure 2 shows the temperature profiles of the rice husk samples in the lab-scale torrefaction device. The sample temperature rose quickly and then was maintained at the torrefaction temperature until the end of the experiment. Thus, the torrefaction time is clear and can be easily determined from the moments when the samples were fed into the quartz reactor until the quartz reactor was moved out from the heating furnace. Although this testing method is simple, it avoids ambiguity in torrefaction time and facilitates analysis of the mechanism.

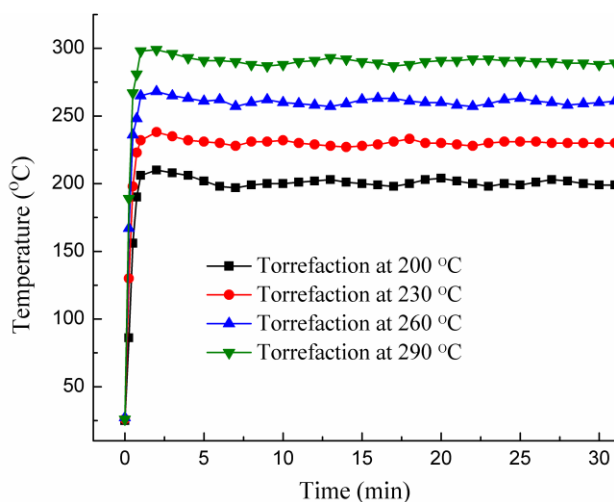


Fig. 2. Temperature profiles of the samples in the lab-scale torrefaction device during torrefaction

Surface Morphology

Figure 3 shows the surface morphology of dried and torrefied rice husk. The mass of samples in each of the containers was 3 ± 0.3 g. As can be seen from Fig. 3, with increasing torrefaction temperature, the surface morphology of torrefied rice husk changed significantly, showing a gradually shrinking volume and turning from yellow to brown and then black.

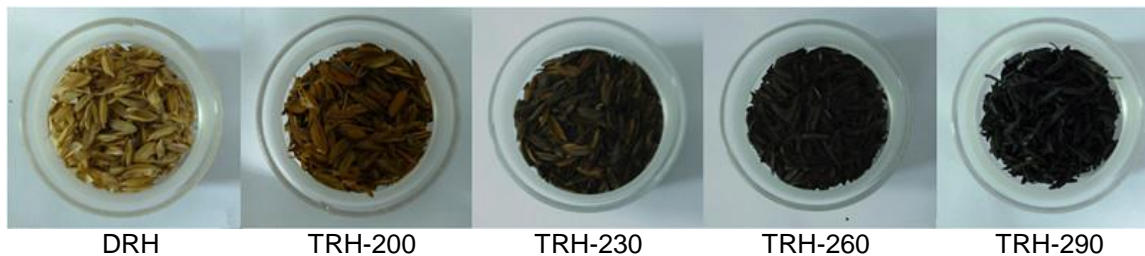


Fig. 3. The effect of torrefaction temperature on the surface morphology of rice husk

Effect of Torrefaction on Chemical Composition

Proximate analysis

The presented method for fuel properties was found to have a good repeatability and accuracy, and the testing results had a maximum relative standard error less than 5%. The average results of proximate analysis, ultimate analysis, higher heating value (HHV) and lower heating value (LHV) of dried and torrefied rice husk are listed in Table 1.

It can be seen from Table 1 that with increasing torrefaction temperature, the amount of volatile matter gradually decreased. The volatiles content was changed little at temperatures of 200 and 230 °C, while a noticeable reduction was observed at torrefaction temperatures of 260 and 290 °C, indicating that high torrefaction temperature had a noticeable influence on the volatile matter content. Similar observations had been found in the study of torrefied pine chips (Phanphanich and Mani 2011) and beechwood chips (Ohliger *et al.* 2013).

During the torrefaction, some volatile matter was released, while ash remained in the solid products, leading to an increase in the ash content of torrefied rice husk with increasing torrefaction temperature. The fixed carbon content of torrefied rice husk also increased with increasing torrefaction temperature.

Table 1. Proximate Analysis, Ultimate Analysis, and Heating Value of Dried and Torrefied Rice Husk

Sample	Proximate analysis (wt.%, db)			Ultimate analysis (wt.%, db)					HHV (MJ/kg)	LHV (MJ/kg)	Bulk density (kg/m ³)
	Volatiles	Fixed carbon	Ash	[C]	[H]	[O]	[N]	[S]			
DRH	64.89	19.83	15.28	42.13	5.40	36.47	0.55	0.17	15.16	13.97	121.5
TRH-200	65.05	19.87	15.09	42.38	5.33	36.45	0.57	0.18	16.63	15.45	120.7
TRH-230	60.78	23.03	16.19	44.17	5.42	33.36	0.69	0.17	16.92	15.77	115.9
TRH-260	54.83	27.64	17.54	46.07	4.86	30.68	0.70	0.15	17.53	16.46	107.3
TRH-290	40.06	37.68	22.26	50.15	4.32	22.38	0.71	0.18	17.95	16.99	96.7

Ultimate analysis

With increasing torrefaction temperature and torrefaction time, the main elements (C, H, N, S, O) of rice husk changed to different degrees. The nitrogen contents were low (less than 1%) and slightly increased with increasing torrefaction. As seen from Table 1, the torrefaction temperature had little effect on the relative content of S; however, the absolute content of sulfur decreased compared with the initial sulfur content in rice husk. The solid yields of torrefied rice husk are given in Fig. 4. If the original dried rice husk (DRH) was 100 g, the absolute content of sulfur in DRH was 0.18 g (100 g × 0.18%), the remain mass of sulfur in TRH-200, TRH-230, TRH-260, and TRH-290 was 0.176 g (100 g × solid yields × 0.18%), 0.157 g, 0.123 g, and 0.120 g, respectively. Knudsen *et al.* (2004) indicated that the release of sulfur begins with the cysteine and methionine units (two main S-containing precursors for plant protein) which start to decompose at 178 and 183 °C, respectively (Knudsen *et al.* 2004). Similar results were found by Saleh *et al.* (2014). In their study, the release of sulfur from straw and miscanthus was approximately 20% at 250 °C and then gradually increased to approximately 50% at 350 °C.

The hydrogen content was basically not reduced during the low-temperature period (200 to 230 °C), and only a slight reduction was detected when torrefaction was carried out at higher temperatures (260 to 290 °C). This is because hydrocarbons, such as

CH₄ and C₂H₆, are only released at higher temperatures. Similar results have been reported for eucalyptus (Arias *et al.* 2008).

The most obvious change is the contents of carbon and oxygen. Carbon content gradually rose and the oxygen content of the torrefied samples underwent a considerable decrease. This was because rice husk underwent decarboxylation and carbonylation reactions during the torrefaction, generating moisture, CO₂, CO, and oxygen-containing carbohydrates. Park *et al.* (2013) suggested that the changes in carbon and oxygen contents are due to the formation and release of CO₂ and CO during the torrefaction process.

Heating value

As can be seen from Table 1, the HHV and LHV of torrefied rice husk noticeably increased with increasing torrefaction temperature. The increase in heating value of rice husk during torrefaction was comparable with other similar studies for agricultural residues (wheat straw and cotton gin waste) (Sadaka and Negi 2009) and wood chips (Meng *et al.* 2012). More moisture and high oxygen content are the primary reasons for the low quality of biomass. The decrease in moisture content and increase in the C/O ratio improves the HHV of the torrefied rice husk compared to the dried rice husk, which will also help enhance the value of rice husk as a raw material for thermo-chemical conversion.

Composition analysis

The effects of torrefaction temperature on the chemical composition of rice husk are shown in Table 2. After torrefaction at 290 °C for 30 min, the amount of hemicellulose was almost undetectable. In other words, the hemicellulose was the major decomposed component. The cellulose content changed slightly in the temperature range of 200 °C to 230 °C. Thus, cellulose did not undergo much decomposition in the torrefaction process. Then, it decreased quickly in the temperature range of 260 °C to 290 °C, indicating that the cellulose started to partially decompose at 260 °C. Although the lignin in the torrefaction process is also decomposed to some extent, due to the large amount of hemicellulose that was decomposed, the relative amount of lignin rose markedly. These results are in accordance with the literature (Phanphanich and Mani 2011; Zheng *et al.* 2012).

The behaviors of the three components are directly related to their chemical structure. Previous studies have indicated that the thermal stability of the three components are lignin > cellulose > hemicellulose. Therefore, the changes in the composition of rice husk during torrefaction involve the decomposition of hemicelluloses and the partial depolymerization of cellulose and lignin.

Table 2. Chemical Composition of Dried and Torrefied Rice Husk

Sample	Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)	Extractives (wt.%)
DRH	40.19	19.69	14.43	10.15
TRH-200	41.43	19.67	14.71	8.71
TRH-230	38.33	7.61	29.66	7.70
TRH-260	26.73	4.36	45.32	5.50
TRH-290	8.90	2.08	62.65	3.39

Effect of Torrefaction on Solid Yield and Energy Yield

Figure 4 shows the effect of torrefaction temperature on the solid yield and energy yield of rice husk. The mass loss of rice husk can be attributed to the release of moisture and volatile matter. During the torrefaction, moisture content was released following two different mechanisms. The first mechanism was the evaporation of moisture content in biomass, and the second one was the dehydration reaction of organic components of biomass.

Torrefaction temperature greatly influenced the solid yield. When the torrefaction temperature was 200 °C, the weight loss was not obvious and the solid yield was 97.4%. The weight loss was caused by the evaporation of moisture content and only a slight decomposition of sample. At 230 °C, the solid yield decreased to 92.3%. At relatively high temperatures of 260 °C to 290 °C, the solid yield dropped at a fast rate. At 290 °C, the solid yield was only 67.0%.

Torrefaction reduced the oxygen content but increased the carbon content of rice husk, thus increasing the heating value of rice husk with increasing temperature. As shown in Fig. 4, the energy yield showed a trend similar to that of the solid yield; they both decreased with increasing torrefaction temperature. Compared with the energy yield, temperature had a more noticeable impact on the solid yield. When the torrefaction temperature was lower than 230 °C, the energy yield was more than 93.9%. When it was higher than 260 °C, most of the hemicelluloses was decomposed, and the cellulose started to decompose, so the solid yield decreased quickly, while the HHV of torrefied rice husk did not increase significantly. Thus the energy yield dropped quickly. At 290 °C, the energy yield was only 72.2%.

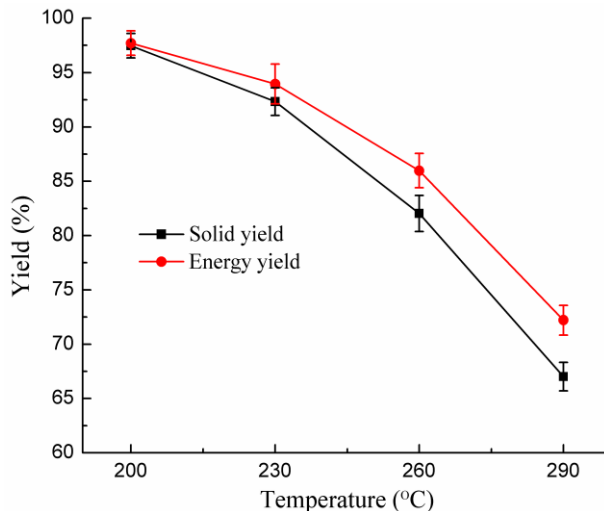


Fig. 4. Effect of torrefaction temperature on the solid yield and energy yield of torrefied rice husk

Effect of Torrefaction on Carbon Yield, Hydrogen Yield, and Oxygen Yield

The carbon, hydrogen, and oxygen yields (Fig. 5) depended on torrefaction temperature (Carbon yield = $C_{wt}\%$ in torrefied rice husk \times Solid yield / $C_{wt}\%$ in dried rice husk). It can be seen from Fig. 5 that at low torrefaction temperature (200 and 230 °C), the torrefied rice husk retained more than 96.8% of carbon in the rice husk; and at high torrefaction temperature (290 °C), there was more than 79.8% of carbon retained in the torrefied rice husk. That is to say, at 290 °C, 20.2% ($100\% - 79.8\% = 20.2\%$) of carbon was volatilized. However, the oxygen yields of torrefied rice husk were very low.

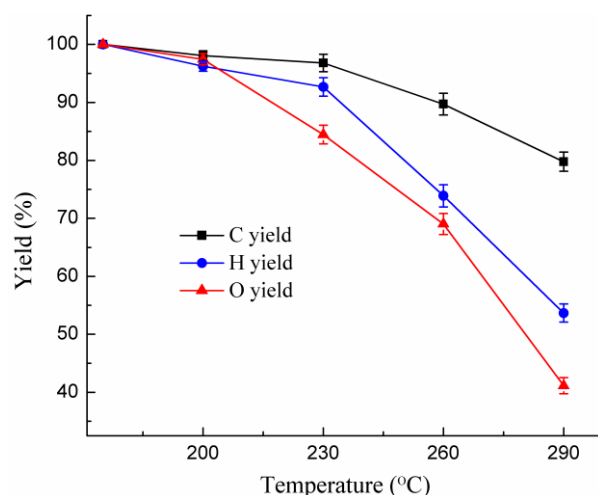


Fig. 5. Effect of torrefaction temperature on the carbon yield, hydrogen yield, and oxygen yield of torrefied rice husk

At low torrefaction temperature (200 and 230 °C), about 2.6% to 15.6% of oxygen was volatilized, while the oxygen volatilized in the torrefied rice husk was as high as about 58.9% at 290 °C. The hydrogen yield was between carbon yield and oxygen yield. Thus, it can be concluded that most of the carbon was retained, while a large proportion of the oxygen is released in the course of torrefaction, which very much contributes to promoting the fuel properties of rice husk.

Effect of Torrefaction on Grindability and Hydrophobicity

Grindability analysis

Figure 6 shows the distribution of particle sizes of dried and torrefied rice husk. It can be seen from Fig. 6 that dried rice husk was hard to shred, and the particle size of rice husk reached the maximum proportion when the sieve number was 40 to 60 mesh (0.38 to 0.25 mm), while reaching the minimum proportion when the sieve number was 140 to 400 mesh (0.109 to 0.038 mm).

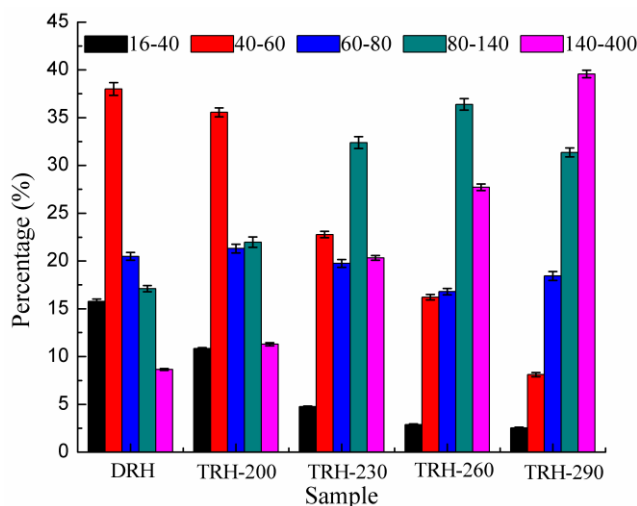


Fig. 6. Effect of torrefaction temperature on the particle size distribution of rice husk

After torrefaction, the particle proportion between 16 and 40 mesh (1 to 0.38 mm) and between 40 and 60 mesh (0.38 to 0.25 mm) decreased noticeably. The particle proportion in the range of 60 to 80 mesh (0.25 to 0.18 mm) remained almost the same as that of the dried rice husk. However, in the 80 to 140 mesh (0.18 to 0.109 mm) and 140 to 400 mesh (0.109 to 0.038 mm) ranges the proportion of particles reached the maximum. In all cases, there was an improvement in the grindability characteristics of the torrefied rice husk. These results indicate that torrefied rice husk became brittle and fragile, and the particle size had a tendency to decrease.

Biomass has a high-fiber structure with closely connected organic components, which makes biomass grinding very difficult (Arias *et al.* 2008). After the torrefaction, the cellulose, hemicelluloses, and lignin in rice husk showed different degrees of decomposition and the tight fiber structure was weakened, leading to a reduced tenacity for rice husk. Thus, torrefaction pretreatment could facilitate the transportation and storage of biomass.

Torrefaction itself is an energy-consuming process (Batidzirai *et al.* 2013). However, the improved grinding performance of rice husk after torrefaction could significantly save power consumption during biomass milling. This might offset the energy consumed in torrefaction to a certain degree and could facilitate the large-scale pyrolysis and liquefaction of biomass.

Hydrophobicity analysis

Equilibrium moisture content (EMC) can be used as an indicator of the hydrophobicity of a solid (Yan *et al.* 2009). Table 3 clearly shows that the EMC of torrefied rice husk decreased with increasing torrefaction temperature, indicating that torrefied rice husk became more hydrophobic.

For lignocellulosic biomass, moisture adheres to the surface of pores in materials and is hydrogen-bonded to the hydroxyl groups of the cell wall components (Andersson and Tillman 1989). The more oxygen present in the lignocellulosic biomass, the greater will be the possibility of forming H-bonds with the H₂O. The ultimate and component analyses showed that a large amount of oxygen was removed and hydroxyl groups in hemicelluloses were broken. The breakdown of these hydroxyl groups after torrefaction results in more hydrophobic torrefied rice husk; thus, the EMC decreased with increasing torrefaction temperature.

The presence of water in biomass negatively affects the pyrolysis products. Thus, drying pretreatment is beneficial before biomass pyrolysis (Chen *et al.* 2013). These dried rice husks need to be in sealed storage or stored in a room with several dehumidifiers to avoid becoming wet again. Rice husk easily absorbs moisture, which leads to biological deterioration in a wet environment. However, torrefied rice husk with low EMC can be stored stably over time with low risk of mold. In addition, torrefaction reduces the specific density of biomass, which may reduce transportation costs.

Table 3. Equilibrium Moisture Content of Dried and Torrefied Rice Husk

Sample	EMC
DRH	9.4%
TRH-200	6.5%
TRH-230	5.2%
TRH-260	4.5%
TRH-290	1.4%

Optimal Torrefaction Conditions

From the EMC results presented in Table 3, as well as those for grindability (Fig. 6), and solid, energy, and carbon yields (Fig. 4 and Fig. 5), it seems that a mild torrefaction treatment at 230 to 260 °C for 30 min is the optimal torrefaction condition for improving the hydrophobicity, heating value, and grinding characteristics of rice husk with little loss of solid and energy yields.

CONCLUSIONS

1. The results of rice husk torrefaction are similar to other biomass materials. A net reduction of the volatiles content, atomic oxygen content, mass yield, and energy yield correlate with increasing temperature, while atomic carbon content and high heating value (energy density) increase with higher torrefaction temperatures.
2. The primary changes in the composition of rice husk during torrefaction involve the decomposition of hemicelluloses and the partial depolymerization of cellulose and lignin.
3. The torrefied rice husk retained more than 79% of carbon in the rice husk. However, the oxygen yields of torrefied rice husk were very low. The oxygen volatilized in the torrefied rice husk was as high as about 60% at 290 °C. The carbon mostly was retained, while a large proportion of oxygen was released in the course of torrefaction, which contributes to promoting the fuel properties of rice husk.
4. Torrefied rice husk became brittle and fragile, and the particle size had a tendency to decrease. Torrefied rice husk with low equilibrium moisture content can be stored stably over time, with low risk of mold.
5. A mild torrefaction treatment at 230 to 260 °C for 30 min is the optimal torrefaction condition for improving the hydrophobicity, heating value, and grinding characteristics of rice husk with little loss of solid and energy yields.

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REFERENCES CITED

- Acharjee, T. C., Coronella, C. J., and Vasquez, V. R. (2011). "Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass," *Bioresource Technology* 102(7), 4849-54.

- Andersson, M., and Tillman, A. M. (1989). "Acetylation of jute: Effects on strength, rot resistance, and hydrophobicity," *J. Applied Polymer Science* 37(12), 3437-3447.
- Arias, B., Pevida, C., Feroso, J., Plaza, M. G., Rubiera, F., and Pis, J. J. (2008). "Influence of torrefaction on the grindability and reactivity of woody biomass," *Fuel Processing Technology* 89(2), 169-175.
- Batidzirai, B., Mignot, A. P. R., Schakel, W. B., Junginger, H. M., and Faaij, A. P. C. (2013). "Biomass torrefaction technology: Techno-economic status and future prospects," *Energy* 62, 196-214.
- Chen, D. Y., Li, K., and Zhu, X. F. (2012a). "Determination of effective moisture diffusivity and activation energy for drying of powdered peanut shell under isothermal conditions," *Bioresources* 7(3), 3670-3678.
- Chen, D. Y., Liu, X., and Zhu, X. F. (2013). "A one-step non-isothermal method for the determination of effective moisture diffusivity in powdered biomass," *Biomass and Bioenergy* 50, 81-86.
- Chen, D. Y., Zhou, J. B., and Zhang, Q. S. (2014). "Effects of heating rate on slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo," *Bioresource Technology* 169, 313-319.
- Chen, W.-H., and Kuo, P.-C. (2010). "A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry," *Energy* 35(6), 2580-2586.
- Chen, W.-H., Lu, K.-M., and Tsai, C.-M. (2012b). "An experimental analysis on property and structure variations of agricultural wastes undergoing torrefaction," *Applied Energy* 100, 318-325.
- Deng, J., Wang, G.-j., Kuang, J.-h., Zhang, Y.-l., and Luo, Y.-h. (2009). "Pretreatment of agricultural residues for co-gasification via torrefaction," *Journal of Analytical and Applied Pyrolysis* 86(2), 331-337.
- Knudsen, J. N., Jensen, P. A., Lin, W. G., Frandsen, F. J., and Dam-Johansen, K. (2004). "Sulfur transformations during thermal conversion of herbaceous biomass," *Energy & Fuels* 18(3), 810-819.
- Medic, D., Darr, M., Shah, A., Potter, B., and Zimmerman, J. (2012). "Effects of torrefaction process parameters on biomass feedstock upgrading," *Fuel* 91(1), 147-154.
- Meng, J., Park, J., Tilotta, D., and Park, S. (2012). "The effect of torrefaction on the chemistry of fast-pyrolysis bio-oil," *Bioresource Technology* 111, 439-446.
- Ohliger, A., Förster, M., and Kneer, R. (2013). "Torrefaction of beechwood: A parametric study including heat of reaction and grindability," *Fuel* 104, 607-613.
- Park, J., Meng, J., Lim, K. H., Rojas, O. J., and Park, S. (2013). "Transformation of lignocellulosic biomass during torrefaction," *Journal of Analytical and Applied Pyrolysis* 100, 199-206.
- Patuzzi, F., Mimmo, T., Cesco, S., Gasparella, A., and Baratieri, M. (2013). "Common reeds (*Phragmites australis*) as sustainable energy source: Experimental and modelling analysis of torrefaction and pyrolysis processes," *GCB Bioenergy* 5(4), 367-374.
- Peng, J. H., Bi, X. T., Sokhansanj, S., and Lim, C. J. (2013). "Torrefaction and densification of different species of softwood residues," *Fuel* 111, 411-421.
- Phanphanich, M., and Mani, S. (2011). "Impact of torrefaction on the grindability and fuel characteristics of forest biomass," *Bioresource Technology* 102(2), 1246-1253.
- Protasio, T. d. P., Bufalino, L., Denzin Tonoli, G. H., Guimaraes Junior, M., Trugilho, P. F., and Mendes, L. M. (2013). "Brazilian lignocellulosic wastes for bioenergy

- production: characterization and comparison with fossil fuels," *BioResources* 8(1), 1166-1185.
- Ren, S. J., Lei, H. W., Wang, L., Bu, Q., Chen, S. L., and Wu, J. (2013). "Thermal behaviour and kinetic study for woody biomass torrefaction and torrefied biomass pyrolysis by TGA," *Biosystems Engineering* 116(4), 420-426.
- Rousset, P., Macedo, L., Commandré, J. M., and Moreira, A. (2012). "Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product," *Journal of Analytical and Applied Pyrolysis* 96, 86-91.
- Sabil, K. M., Aziz, M. A., Lal, B., and Uemura, Y. (2013). "Effects of torrefaction on the physiochemical properties of oil palm empty fruit bunches, mesocarp fiber and kernel shell," *Biomass and Bioenergy* 56, 351-360.
- Sadaka, S., and Negi, S. (2009). "Improvements of biomass physical and thermochemical characteristics via torrefaction process," *Environ. Prog. Sust. Energy* 28(3), 427-434.
- Saleh, S. B., Flensburg, J. P., Shoulaiifar, T. K., Sárossy, Z., Hansen, B. B., Egsgaard, H., DeMartini, N., Jensen, P. A., Glarborg, P., and Dam-Johansen, K. (2014). "Release of chlorine and sulfur during biomass torrefaction and pyrolysis," *Energy & Fuels* 28(6), 3738-3746.
- Shang, L., Ahrenfeldt, J., Holm, J. K., Barsberg, S., Zhang, R.-z., Luo, Y.-h., Egsgaard, H., and Henriksen, U. B. (2013). "Intrinsic kinetics and devolatilization of wheat straw during torrefaction," *Journal of Analytical and Applied Pyrolysis* 100, 145-152.
- Tran, K.-Q., Luo, X., Seisenbaeva, G., and Jirjis, R. (2013). "Stump torrefaction for bioenergy application," *Applied Energy* 112(SI), 539-546.
- van der Stelt, M. J. C., Gerhauser, H., Kiel, J. H. A., and Ptasinski, K. J. (2011). "Biomass upgrading by torrefaction for the production of biofuels: A review," *Biomass and Bioenergy* 35, 3748-3762.
- Wang, G. J., Luo, Y. H., Deng, J., Kuang, J. H., and Zhang, Y. L. (2011). "Pretreatment of biomass by torrefaction," *Chinese Science Bulletin* 56(14), 1442-1448.
- Wannapeera, J., Fungtammasan, B., and Worasuwannarak, N. (2011). "Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass," *Journal of Analytical and Applied Pyrolysis* 92(1), 99-105.
- Wannapeera, J., and Worasuwannarak, N. (2012). "Upgrading of woody biomass by torrefaction under pressure," *J. Analytical and Applied Pyrolysis* 96, 173-180.
- Yan, W., Acharjee, T. C., Coronella, C. J., and Vásquez, V. R. (2009). "Thermal pretreatment of lignocellulosic biomass," *Environmental Progress & Sustainable Energy* 28(3), 435-440.
- Yin, R. Z., Liu, R. H., Wu, J. K., Wu, X. W., Sun, C., and Wu, C. (2012). "Influence of particle size on performance of a pilot-scale fixed-bed gasification system," *Bioresource Technology* 119, 15-21.
- Zheng, A. Q., Zhao, Z. L., Chang, S., Huang, Z., He, F., and Li, H. B. (2012). "Effect of torrefaction temperature on product distribution from two-staged pyrolysis of biomass," *Energy & Fuels* 26(5), 2968-2974.
- Zheng, A. Q., Zhao, Z. L., Chang, S., Huang, Z., Wang, X. B., He, F., and Li, H. B. (2013). "Effect of torrefaction on structure and fast pyrolysis behavior of corncobs," *Bioresource Technology* 128, 370-377.

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